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(54) Title: ARTICLES EXHIBITING DURABLE COLOUR AND/OR FLUORESCENT PROPERTIES (57) Abstract An article exhibiting durable fluorescent properties comprising a polymeric matrix, dye, and hindered amine light stabilizer, wherein the polymeric matrix is comprised of polycarbonate and the dye is comprised of a dye selected from the group consisting essentially of thioxanthone, perylene imide and/or thioindigoid compounds. The article exhibits durable fluorescence which resists degradation by ultraviolet or visible radiation. The invention is optionally combined with retroreflective elements so that the resultant article has durable fluorescent properties when exposed to sunlight and is also retroreflective. A method of manufacturing an article exhibiting durable fluorescent properties is also disclosed along with a method of increasing the durability of polycarbonate in a dyed system.		

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ARTICLES EXHIBITING DURABLE COLOUR AND/OR FLUORESCENT PROPERTIES

Field of the Invention

The present invention relates to articles having increased
5 color and/or fluorescent durability.

Background

It is commonly known that ultraviolet radiation causes
colorants to degrade. This is a particularly acute problem for articles exposed to
10 solar radiation for extended periods of time such as articles placed outdoors. Color
degradation occurs in articles colored with conventional colorants as well as articles
colored with fluorescent colorants. However, this is a particularly acute problem
for fluorescent articles. Fluorescent dyes degrade, often turning colorless more
quickly than conventional colorants. The effective life of fluorescent materials
15 exposed to daily solar radiation is short and is typically measured in terms of days
or months. In contrast, the life of conventionally colored materials is usually
substantially longer and is typically measured in years.

If increased visibility of an article is desired, the article is
often colored with fluorescent colorants even though fluorescent colorants are less
20 durable than conventional colorants. Fluorescent colors allow enhanced visibility
because the visual contrast that the fluorescent colors create with the environment
make the materials more conspicuous than ordinary nonfluorescent articles. An
example of one industry which benefits from using fluorescent colorants is the
traffic sign industry. Fluorescent colored traffic signs are effective at increasing the
25 visibility of the signs which increases motorist safety. Even though fluorescent
signs increase motorist safety, their use has been limited due to their poor color
stability and the need to frequently replace them to maintain effective performance.

At ground level, solar radiation comprises electromagnetic
radiation having wavelengths longer than about 290 nanometers, with the range
30 from about 400 to about 700 nanometers typically considered the visible light range.
Radiation having shorter wavelengths than visible light is believed to be damaging

to both conventional and fluorescent colorants. Attempts to maintain color of a fluorescent article have included adding ultraviolet screens which selectively filter radiation below the 340 nm to 380 nm range. Japan Kokai No. 2-16042, Application No. 63-165914 (Koshiji, et al.) discloses fluorescent articles comprising a screen layer and a layer containing a fluorescent coloring agent wherein the screen layer only permits a defined range of light transmission. European Patent Application No. 91311189.4 also discloses a retroreflective article comprising an ultraviolet screening layer and a color layer contained in a defined polymeric matrix. The article exhibits durable daylight fluorescence and resistance to degradation from exposure to sunlight.

Articles which exhibit enhanced fluorescence and color durability, even when exposed to ultraviolet radiation, are needed. In particular, fluorescent articles which retain their color and/or their fluorescent properties without requiring the use of protectant overlays are needed.

15

Summary of the Invention

The present invention provides, in brief summary, articles which exhibit both enhanced color durability and fluorescing properties with or without the use of protectant overlays. That is, the articles of the invention retain their color and are able to fluoresce for a longer period than is normally expected even when the articles are exposed to direct sunlight. The invention further includes a method to manufacture such durable fluorescent articles. Also included is a method of increasing the durability of polycarbonate in a dyed system.

Articles of the invention comprise (1) polymeric matrix, (2) dye, and (3) hindered amine light stabilizer, wherein the polymeric matrix is comprised of polycarbonate and the dye contains at least one the of compounds selected from the group of thioxanthone, perylene imide, and thioindigoid dyes. The hindered amine light stabilizer is comprised of compounds from the 2,2,6,6-tetraalkyl piperidine class of compounds in a preferred embodiment.

In one embodiment, articles of the present invention also include retroreflective elements. The resulting articles exhibit retroreflective and

5 durable color and/or durable fluorescent properties. Such materials exhibit enhanced daytime and nighttime visibility over the course of extended outdoor exposure.

5 Brief Description of the Drawings

The invention is further explained with reference to the drawings, wherein:

Figure 1 is a cross-sectional view of an embodiment of the invention including retroreflective elements,

10 Figure 2 is a cross-sectional view of an alternate embodiment of the invention including retroreflective elements,

Figure 3 is a cross-sectional view of an alternate embodiment of the invention including retroreflective elements, and

15 Figure 4 is a cross-sectional view of an alternate embodiment of the invention including an ultraviolet protectant overlay and retroreflective elements.

These figures, which are idealized, are not to scale and are intended as merely illustrative and non-limiting.

20 Definitions

As referred to herein, the term "colorant" shall mean pigment or dyes or other substances used to impart hue and chroma and value to an article.

As referred to herein, the term "conventional colorant" shall mean colorants which do not exhibit fluorescent properties to the unaided eye.

25 As referred to herein, the term "durable" shall refer to an enhanced retention of color or fluorescence upon exposure to weathering.

As referred to herein, the term "hindered amine light stabilizer" refers to sterically hindered amines of the class of compounds typically represented by 2,2,6,6 tetraalkyl piperidines.

As referred to herein, the term "weathering" shall mean exposing an article to either natural or artificial environments which include heat, light, moisture, and ultraviolet radiation.

5 Detailed Description of
Illustrative Embodiments of the Invention

The present invention combines a polymeric matrix containing dye and hindered amine light stabilizer to create an article which exhibits enhanced color durability and/or more durable fluorescence. The polymeric matrix of the invention is first discussed followed by a discussion of suitable dyes and of suitable hindered amine light stabilizers.

Polymeric Matrix

Polycarbonate is the preferred polymeric matrix of the invention because it is substantially transparent and is easily colored with fluorescent and conventional dyes. Additionally, polycarbonate exhibits good optical properties such as good light transmittance which is important for the present invention. Even though polycarbonate exhibits these desirable characteristics, it is surprising that polycarbonate is the polymeric matrix of choice for the present invention. As is commonly known in the art, polycarbonate is photosensitive and degrades when exposed to ultraviolet radiation.

Dye

In a preferred embodiment the fluorescent dyes of the invention are dyes from the thioxanthone, perylene imide and thioindigoid classes of compounds. The invention anticipates that a single fluorescent colorant or dye may be used to color an article of the invention or that a combination of one or more fluorescent colorants and one or more conventional colorants may be used.

Typically, between about 0.01 and about 2.00 weight percent, and preferably between about 0.05 and about 0.70 weight percent and most preferably between about 0.1 and about 0.5 weight percent of fluorescent dye is

contained in the article of the present invention. It will be understood that articles with dye loadings outside this range can be used in accordance with the invention. Although dye loading may vary depending upon the final application, these loadings are typical for about a 0.075 to 0.25 mm thick film. However, if the dye is added to
5 a thicker film, lower dye loadings can give the same visual effect. As known by those in the art, articles having heavier dye loadings will exhibit brighter fluorescence and/or deeper color than will articles with lighter dye loadings of the same dye. However, articles having very high fluorescent dye loadings may exhibit a self-quenching phenomenon which occurs when molecules of the fluorescent dye
10 absorbs the energy emitted by neighboring fluorescent dye molecules. This self-quenching causes an undesirable decrease in fluorescent brightness.

In some embodiments, the colorant in the articles of the present invention will consist essentially of one or more dyes selected from the perylene imide, thioindigoid and thioxanthone classes of compounds. In other
15 instances, the article may also contain other coloring agents such as pigments or other dyes in addition to those described to adjust the color and appearance of the article. For example, polycarbonate typically has a yellow cast. Minor amounts, e.g., about 0.01 weight percent or less, of pigments sometimes referred to as "bluing agents" may be incorporated to neutralize the yellow appearance. Other
20 non-fluorescent or conventional dyes or pigments may also be added to the present invention, however, care should be taken in selecting such dyes and dye loadings so that the dyes do not significantly interfere with the performance of the fluorescent dyes. If retroreflective elements are included in the article of the present invention, any dyes or pigments should not undesirably impair the transparency of the article
25 as such would impair the retroreflective properties of the article.

Hindered Amine Light Stabilizers

Hindered amine light stabilizers (HALS) are included in the article of the present invention. This is a somewhat surprising combination because, as one skilled in the art will recognize, it is not recommended to combine amines with polycarbonate. It has traditionally been known that amines attacked the carbonyl group of the polycarbonate, thereby degrading the polycarbonate (for example see Schnell, Chemistry and Physics of Polycarbonates, page 183, 1964).

Without intending to be bound by theory, it is believed that the combination of the sterically hindered amine, the polycarbonate matrix and the dye in the present invention prevents an as yet undefined degradation and/or reaction between the dye and the polycarbonate which could otherwise occur. Insofar as we know, the advantages of the present invention are attained through the combination of dye, polymer matrix material, and hindered amine light stabilizer described herein. The dyes in the present invention are thought to act as singlet oxygen sensitizers. Energy transfer, which generally occurs from the triplet state of the dye, is quenched by ground state molecular oxygen to produce active singlet oxygen. The singlet oxygen is then free to react with the dye, causing dye degradation. Alternatively, the singlet oxygen may react with the polymer, leading to degradation of the polycarbonate. However, the hindered amine light stabilizer present in the invention is capable of directly quenching the singlet oxygen formed, preventing initiation of the degradation reactions. The hindered amine light stabilizers can also prevent secondary reactions initiated by polymer oxidation from proceeding. These reactions include a number of radical or peroxide-based chain reactions that are thought to occur in the photo-oxidation of polycarbonate which can result in polymer and dye degradation. Preventing these reactions increases the durability of the polycarbonate and the dye in the dyed system.

Any hindered amine light stabilizer is suitable for the present invention such as 2,2,6,6 tetraalkyl piperidine compounds but preferably 2,2,6,6 tetramethyl piperidine compounds are employed as the hindered amine light stabilizers due to the ready availability of the compounds. The hindered amine light stabilizers are included in articles of the present invention from about 0.05 to about

1.00 weight percent and preferably from about 0.10 to about 0.75 weight percent and most preferably from about 0.1 to about 0.5 weight percent.

Retroreflection

As previously stated, in some embodiments articles of the present invention are retroreflective. Such retroreflective capability is important when using the present invention to make traffic signs. Figure 1 illustrates how retroreflective capability can be achieved in the present invention by forming retroreflective elements 30 on one side of a film 32 containing the polymeric matrix/hindered amine/dye composite. Figures 2 and 3 illustrate alternate retroreflective embodiments of the invention. A retroreflective base sheet 12 or 40 is attached to a sheet 18 or 50 of the present invention by either mechanically laminating the retroreflective base sheet and the invention sheet directly to each other, or by attaching the two sheets with a transparent adhesive. If an adhesive is used, the adhesive is preferably substantially transparent to visible light. As shown in Figure 2, the retroreflective base sheet may comprise cube-corner retroreflective elements 20 formed on the back side of the sheet. Other embodiments include a base sheet 40 having microsphere-based retroreflective structures 52 as illustrated in Figure 3. A monolayer of microspheres 71 is embedded in binder layer 70 with space layer 72, specular reflective layer 74 and optional adhesive 76. Examples of retroreflective elements are disclosed in U.S. Patent Numbers 4,896,943 and 5,069,964 (both microsphere-based structures) and 4,938,563 (cube-corner reflector structure).

25 : Ultraviolet Protectant Overlays

Although not necessary, articles of the present invention may optionally include an overlay which may or may not include ultraviolet absorbing agents. Some additional improvement in resisting degradation is observed when the article of the present invention is covered by an overlay including ultraviolet
30 absorbing agents and is exposed to sunlight. The overlay is preferably substantially transparent to visible light and includes a means to screen substantial portions of

incident ultraviolet radiation. Figure 4 illustrates a retroreflective embodiment of the present invention similar to that shown in Figure 2 and further including an overlay 56. The polymeric matrix/dye/hindered amine light stabilizer composite is shown as a film 60 and is laminated to a cube-corner retroreflective sheet 64. The overlay 56 is preferably coextensive with the composite film 60 so as to provide the most protection to the invention film 60.

Examples

The invention is further explained by the following illustrative examples which are intended as nonlimiting. Unless otherwise indicated, all amounts are expressed in parts by weight.

The following abbreviations are used in the examples:

<u>Abbreviation</u>	<u>Meaning</u>
PC	Polycarbonate;
PMMA	
Polymethylmethacrylate;	
SO63	HOSTASOL RED GG™ - Solvent Orange 63 thioxanthone dye from
RED 41	Hoechst Celanese; HOSTASOL RED 5B™ - Vat Red 41 thioindigoid dye from Hoechst Celanese;
PI 240	LUMOGEN F240™ Orange - perylene imide dye from BASF;
SY 160:1	MACROLEX 10GN™ Solvent Yellow 160:1 benzoxazole coumarin dye from Mobay Corp.
SG 5	FLUOROL GREEN GOLD 084™ Solvent Green 5 perylene dye from BASF.

	HALS1	Dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1- piperidine ethanol available as TINUVIN 622 from Ciba-Geigy Corp, Hawthorne, NY.
5		
	HALS2	Poly [6[(1,1,3,3- tetramethylbutyl) amino]-s-triazine- 2,4-diyl] [2,2,6,6-tetramethyl-4- piperidyl) imino] hexamethylene [(2,2,6,6-tetramethyl-4-piperidyl) imino]] available as CHIMASORB 944FL from Ciba-Geigy Corp.
10		
	HALS3	bis (2,2,6,6-Tetramethyl-4- piperidiny) sebacate available as TINUVIN 770 from Ciba-Geigy Corp.
15		

Unless otherwise indicated, the following test methods were
used.

20

Accelerated Weathering

In order to simulate outdoor exposure to sunlight on an
accelerated basis, the samples in Examples 1 through 6 and 8 were exposed in
accordance to ASTM G 26 - Type B, Method A, with a water-cooled xenon arc
device with borosilicate inner and outer filters for periods of 102 minutes of
exposure at a Black Panel temperature of about 63°C followed by 18 minutes of
exposure while subjecting the sample to deionized water spray. One thousand
hours exposure in this cycle is believed equivalent to at least several months
exposure to direct outdoor sunlight.

30

Color

Color was determined by the following technique.

A Labscan 6000 Spectrophotometer from Hunter was used at the following settings and conditions:

- 5 Illuminant D₆₅ ,
- 0/45 Geometry,
- 25 millimeter port,
- CIE 2 Degree Standard Observer,

- 10 with measurements taken every 10 nanometers over a range of 400 to 700 nanometers.

- Percent of Initial Peak Total Spectral Radiance Factor (%PTSR) was calculated as the ratio, in percent, of peak total spectral radiance factor of the sample after exposure for the indicated time (time t) to the peak total spectral radiance factor of an unexposed sample at the wavelength of the initial peak total spectral radiance. This is better illustrated by the following equation.

$$\begin{aligned} &\%PTSR = \\ &\frac{\text{Peak Total Spectral Radiance of exposed}}{\text{Peak Total Spectral Radiance of unexposed}} \times 100 \end{aligned}$$

- 20 Peak total spectral radiance factor is a relative measure of the fluorescence content. Fluorescence content is directly correlated to the amount of fluorescent dye, therefore, peak reflectance is a relative measure of the fluorescent dye content remaining. Difference in % PTSR of about 5 or less are generally not considered as significant for measurements made on constructions.

- The CIELAB color difference, (or DE*), between the sample after exposure for the indicated period of time and the unexposed sample was determined. DE* is a function of several color vector components. For purposes of reference only, a DE*, or color change of about 2 units is just detectable by the naked eye whereas a DE* of 20 or greater represents a substantial color change.

Retained Fluorescence

Fluorescence was measured using a SLM AB2 Luminescence Spectrophotometer (SLM Instruments, Rochester, NY) using a 150 watt continuous Xenon lamp.

Retained Fluorescence was calculated as the ratio, in percent, of fluorescent intensity of the sample after exposure for the indicated length of time to the fluorescent intensity of an unexposed sample, at the wavelength of peak emission of the unexposed sample.

Molecular Weight

Molecular weight was measured by gel permeation chromatography (GPC) using a set of MICROSTYRAGEL brand columns available from Waters Division of Millipore Corp, Milford, MA and polystyrene standards for calibration. Samples were dissolved and run in tetrahydrofuran at 30°C at a flow rate of 1.0 milliliter per minute. A UV detector set at 266nm was used for detection of polycarbonate.

Exterior Weathering

Exterior weathering was done on samples about 7 X 12 centimeters in size. The samples were adhered to an aluminum coupon which was mounted on a black painted panel facing upward at 45° from vertical and facing south. The samples were exposed for 12 months in Wittmann, Arizona.

Determining Time to 50% Dye Loss

Films were mounted onto aluminum slide frames, overlaid with an ultraviolet transparent polyolefin film which was a 2 mil (0.005 cm) thick film of an ethylene/acrylic acid copolymer made from Primacor 3440 available from Dow Corporation of Midland, MI and exposed in accordance with ASTM G26, Type B, Method A, as described earlier.

The dye concentration in each sample was measured initially and after every 500 hours exposure. The samples were exposed for a total of 2000

hours. The Time-to-50%-Dye-Loss for each sample was graphically interpolated from plots of dye concentration versus total exposure (ie. [SO63] vs Hours).

Dye concentrations were determined from UV-Visible spectroscopic measurements of the sample films using the Beer-Lambert Law. All measurements were made on a Beckman Model DU-70 UV Visible Spectrophotometer.

Example 1

Example 1 illustrates the improved durability of fluorescent properties and color of fluorescent dye SO63 with a hindered amine light stabilizer and compares the durability of a sample with a sample including an ultraviolet protectant overlay.

Films were prepared for Example 1 as follows. The fluorescent dye and HALS (if present) were blended with polycarbonate resin pellets. The fluorescent dye was added to the polycarbonate resin pellets at 0.2 weight percent loading. The hindered amine light stabilizer, if present, was incorporated into the mixture at 0.26 wt % loading. The resin pellets used were Makrolon FCR-2407 available from Miles Inc. of Pittsburgh, PA. The dye/resin/HALS mixture was dried overnight to remove moisture. After drying overnight, the mixture was extruded into film of about 4-6 mils (0.1-0.15 mm) thick using a single screw extruder with three heating zones set at 260°C, 260°C and 304°C and a film die set at 304°C. The extruder was a ¾ inch single screw extruder for the Haake Rheocord as available from Haake of Karlsruhe, Germany.

The film was then laminated onto 3M Brand Scotchlite™ Diamond Grade Retroreflective Sheeting 3970G construction (as manufactured by 3M Company of St. Paul, Minnesota) using a transparent acrylic adhesive. An overlay film consisting of urethane-acrylic film with or without a UV absorber as (indicated in the Table 1) was laminated over the fluorescent/retroreflective construction with acrylic adhesive.

The hindered amine light stabilizer (HALS) used for Example 1 samples was HALS 1 (Tinuvin 622), an oligomeric tertiary amine. Comparable

films without HALS were also prepared as described earlier and laminated to form samples having a fluorescent/retroreflective/overlay constructions and all samples were weathered in accelerated test devices as described above. Fluorescence and color retention were assessed by color measurements on the Hunter Labscan 6000.

- 5 Fluorescence durability is correlated to %PTSR and color change is calculated by DE^* described above.

TABLE 1

			% of Initial Peak Spectral Radiance Factor Accelerated exposure in Hours			
Sample ¹	HALS ²	UV Absorber ³	500	1000	1500	2000
1-A	Yes	No	86%	80%	68%	61%
1-B	No	No	80%	60%	54%	43%
1-C	Yes	Yes	90%	84%	80%	63%
1-D	No	Yes	87%	73%	63%	46%

- 10 ¹ All Samples contained dye SO63 at 0.2 wt % loading
² HALS 1 at 0.26 wt % loading
³ UV absorber was Uvinol 400 from BASF at 3 wt% loading.

TABLE 2

			DE^* of Samples Exposed 1000 Hours to Accelerated Exposure as Compared to Unexposed Samples			
Sample ¹	HALS ²	UVA ³	500	1000	1500	2000
1-A	Yes	No	5.7	12.4	26.6	38.2
1-B	No	No	9.9	30.7	35.8	53.8
1-C	Yes	Yes	4.9	13.1	17.8	47.2
1-D	No	Yes	5.5	23.0	32.1	58.6

- 15 ¹ All samples contain dye SO63 at 0.2 wt% loading
² HALS 1 at 0.26 wt% loading
³ Urethane-acrylic overlay with 3% Uvinol 400 (UV absorber) in overlay.

The results shown in Tables 1 and 2 illustrate that the HALS offers a substantial improvement in fluorescence and color durability of SO63 with or without an ultraviolet protectant overlay. The samples containing HALS showed an improvement in color and fluorescence durability as compared to those samples without HALS. Additionally, an improvement was observed in the HALS-containing samples when a UV absorbing overlay was added to the sample.

Example 2

Example 2 illustrates the improved durability of fluorescent properties of dye RED41 in articles of the present invention.

Samples 2E through 2H of Example 2 were prepared as described in Example 1 except that the polycarbonate resin used was Lexan 123R-112 as available from GE Plastics of Mt. Vernon, IN. The hindered amine light stabilizer used for the samples in Example 2 was HALS 1. Samples were weathered using accelerated-weathering devices for the time periods noted. The results are recorded in Table 3 below.

TABLE 3

Sample ¹	HALS ²	% of Initial Peak Total Spectral Radiance Factor For exposure in Hours		
		UVA ³	500	1000
2-E	No	No	81%	53%
2-F	Yes	No	76%	63%
2-G	No	Yes	92%	62%
2-H	Yes	Yes	91%	77%

¹ Samples 2E-2H include dye Red 41 at 0.2 wt% loading

² HALS 1 at 0.26 wt% loading.

³ Urethane-acrylic overlay with 3% Uvinol 400.

The results shown in Table 3 show that the dye RED41 benefits by adding HALS1 (Samples 2-F and 2-H)

Example 3

5 Example 3 illustrates different hindered amine stabilizers at different loadings are suitable for increasing the durability of fluorescent dye SO63.

Films were prepared as described in Example 1. The amount and type of HALS and dye added to each film is designated in Table 4 below. The Samples were exposed in an accelerated weathering device as described earlier.

10

TABLE 4

Sample*	Film Caliper (mm)	Initial Weight % SO63	Additive/Weight %	Time to 50% Dye Loss
CONTROL	0.1	0.2	None	420 hours
3A	0.1	0.2	HALS 2 /0.25%	800 hours
3B	0.1	0.2	HALS 2 /0.5%	740 hours
3C	0.1	0.2	HALS 1 /0.5%	550 hours

15 The results in Table 4 illustrate that different hindered amine light stabilizers, including HALS 2 and HALS 1, are effective at increasing the durability of SO63 fluorescent dye.

Example 4

20 Example 4 illustrates a range of dye loadings is suitable for the present invention.

Samples were prepared as described in Example 3. Dye SO63 and HALS 1 were used to prepare the samples. In samples containing HALS, 0.50 wt percent HALS 1 was included. The amount of dye added to each

sample is listed below. The samples were weathered by exposing them to accelerated weathering.

TABLE 5

Sample	Film Caliper (mm)	Initial Weight % SO63	HALS/ Weight %	Time to 50% Dye Loss
CONTRO L	0.1	0.2	None	420 hours
3C	0.1	0.2	HALS 1 /0.5%	550 hours
4A	0.1	0.4	HALS 1 /0.5%	570 hours

5

The results in Table 5 demonstrate that HALS is effective at different dye loadings.

10

Example 5

Example 5 illustrates different hindered amine light stabilizers with a range of loadings are suitable for the present invention.

Films were prepared as described in Example 1. The resin used was Makrolon FCR-2407 from Miles Incorporated of Pittsburgh, PA. Samples were prepared by hot laminating the colored films to a clear layer with retroreflective elements embossed in a second side and hot laminating a PMMA overlay layer to the first side of the colored films. All colored films contained dye SO63 at 0.20 weight percent. HALS 1 was added to the films as designated in Table 6 below. The samples were weathered by exposing them in an accelerated device for 1000 hours. Results are shown in Table 6.

15

20

TABLE 6

		% PTRSF and DE* for Accelerated Weathering for 1000 Hours			
Sample	[SO63] wt %	HALS	[HALS] wt %	DE*	%PTRSF
5A	0.2	--	0	17.3	75%
5B	0.2	HALS 1	0.1	9.8	89%
5C	0.2	HALS 1	0.25	5.9	89%
5D	0.2	HALS 1	0.5	6.8	90%

- 5 The results illustrate HALS 1 is effective at a variety of loadings for increasing the durability of the fluorescent properties of dye SO63.

Comparative Example 6

- 10 Comparative Example 6 illustrates polymethyl methacrylate is not a suitable polymeric matrix for manufacturing articles of the present invention because such articles do not exhibit increased durability of fluorescent properties or color.

- 15 The films for Comparative Example 6 were prepared as described in Example 1 except the polymeric matrix used was polymethyl methacrylate (PMMA) instead of polycarbonate. The PMMA used was either Perspex CP924 or CP923 from ICI Acrylics (St. Louis, MO) or Lucite 47K from Dupont (Wilmington, DE), all contained roughly 0.3 wt% UV absorber of a benzotriazole type. The HALS used (if any) was HALS 1 added at a loading of 0.25 weight percent. Extrusion temperatures for the PMMA were 249° to 260°C.
- 20 Samples were prepared by hot laminating either four 3 mil (0.075 mm) colored films or two 6 mil (0.15 mm) colored films together and embossing retroreflective elements on the second side of the laminated construction. The samples were weathered by exposing them to accelerated weathering for the times listed in Table 7.

TABLE 7

% of Initial Peak Total Spectral Radiance Factor for Exposure in Hours for PMMA ¹				
Sample	Dye ²	HALS ³	500 Hrs	1000 Hrs
6A	SO63	Yes	74%	72%
6A-1	SO63	No	85%	78%
6B	Red 41	Yes	66%	61%
6B-1	Red 41	No	70%	63%
6C	PI 240	Yes	93%	92%
6C-1	PI 240	No	89%	90%

5

¹ Polymethyl methacrylate

² Dye was added to the samples at a loading of 0.20 weight percent except sample 6C-1 which was at 0.29 weight percent

³ HALS 1 was added at 0.25 wt percent

10

As discussed above, no increase of fluorescence or color durability is observed (Table 7) when adding a HALS and a fluorescent dye to polymethyl methacrylate.

15 Example 7

Example 7 illustrates that polycarbonate is more durable if a hindered amine light stabilizer is included along with the polymeric matrix and a fluorescent dye.

The samples for Example 7 were prepared as described in
 20 Example 5. The resin used was Makrolon FCR-2407 from Miles Inc. Dye SO63 was added to the samples at a loading of 0.2 weight percent. The hindered amine light stabilizer and the amount added to each sample is listed below in Table 8. The samples were weathered by exterior exposure for 12 months as described above.

TABLE 8

Sample	HALS	Weight % HALS	Polycarbonate Number Average Molecular Weight		DE* (vs Unexposed)	Peak Total Spectral Radiance Factor Retained (% of Initial)
			Unexposed	Exposed		
Control	None	0	17,796	12,058	62	55
7-A	HALS 2	0.25	17,687	15,865	19	87
7-B	HALS 2	0.50	17,836	15,552	20	87
7-C	HALS 3	0.50	17,934	15,311	35	77

5

The molecular weight results shown in Table 8 illustrate the polycarbonate and fluorescent dye samples containing HALS did not degrade as readily as the control which did not contain HALS. Thus, the present invention helps to increase the durability of polycarbonate.

10

The results in Table 8 further show that the colors and the fluorescent properties in the samples containing the HALS did not change color as readily as the samples which did not contain the HALS.

Example 8

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Example 8 illustrates the effect of several different hindered amine light stabilizers on fluorescent color durability on outdoor exposure.

Samples were prepared as in Example 5, except that a second color layer was used in place of the clear layer and it was embossed with retroreflective elements. The resin used was Makrolon FCR-2407 from Miles Inc.

20

All colored films contained dye SO63 at 0.25 wt percent in polycarbonate, the hindered amines added are designated in Table 9 and were added at 0.25 wt percent. The samples were exposed in Arizona for 1 year as described earlier and

measurements were taken for Percent of Initial Peak Total Spectral Radiance and color change. The color change results are given in Table 9.

TABLE 9

5

Sample	Arizona Exposure 12 months		
	HALS ADDED	% PTSRF	Color Change (DE [*])
Control	None	43	48
8-A	HALS 1	70	21
8-B	HALS 2	83	9.6
8-C	HALS 3	89	14

Example 9

Example 9 illustrates the enhanced fluorescence durability of samples of the present invention as measured by a spectrofluorometer. Samples were prepared as in Example 5 and exposed to accelerated weathering. Readings were taken initially and at 2500 hours. The HALS, the dye and the respective loadings are listed in Table 10 below along with the results.

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TABLE 10

Sample	[HALS]	Dye [SO63]	% Retained Fluorescence	DE*	% PTSRF
Control 9A ¹	0	0.2 wt %	31%	68.6	48%
9B ¹	HALS 2 / 0.25 wt %	0.2 wt %	78%	34.8	77%
Control 9C ²	0	0.2 wt %	26%	71.3	42%
9D ²	HALS 3 / 0.25 wt %	0.2 wt %	81%	32.3	81%

¹ Polycarbonate was comprised of Makrolon 2407

² Polycarbonate was comprised of 80% Makrolon 2407 and 20% Lexan

5 123R

Comparative Example 10

Comparative Example 10 illustrates that fluorescent dyes SY 160:1 and SG 5 are not suitable dyes for the present invention. Films were prepared as described in Example 1. Samples 10A, 10B and 10D were prepared by hot laminating two 4 mil (0.1 mm) colored films together. A 2 mil PMMA overlay containing 1.8% Tinuvin 327 (UV absorber available from Ciba-Geigy) was hot laminated to a first side of the colored laminate. Sample 10C was prepared by hot laminating a 3 mil PMMA overlay containing 1.2 weight percent Tinuvin 327 to a first side of a 12 mil (0.3 mm) film and embossing retroreflective elements in the second side of the film. The polycarbonate resin used in Samples 10A and 10B was Makrolon 2407 and Lexan 123R-112 was used in Samples 10C and 10D.

Samples 10E and 10F are samples which are provided for comparison purposes. Samples 10E and 10F are prepared according to the present invention and demonstrate that perylene imide dyes are suitable for use in the present invention. Sample 10E was formed from polycarbonate resin Lexan 123R-112. A 12 mil polycarbonate film was formed with a 3 mil (0.075 mm) PMMA overlay hot laminated to the first side of the colored film with retroreflective elements embossed into the second side of the colored film. Sample 10-F was formed from polycarbonate resin Lexan 123R-112. The sample was prepared by hot laminating two 4 mil (0.10 mm) colored films together and by laminating a 2 mil (0.05 mm) PMMA overlay to a first surface of the resulting colored film. Retroreflective elements were embossed into the second surface of the colored film. The overlays for samples 10-E and 10-F were made to have the same UV screening ability. The 3 mil (0.75 mm) overlay included 1.2 wt % Tinuvin 327 as available from Ciba Geigy Corp. while the 2 mil (0.05 mm) overlay contained 1.8 wt % Tinuvin 327. The HALS used for all the samples was HALS1. The samples were weathered by exposing them to accelerated weathering. Results are given in Table 11.

TABLE 11

Sample	[DYE] wt %	[HALS] wt %	1000	1500	2000
10A	SY160:1 0.2	--	82%	79%	67%
10B	SY160:1 0.2	0.25	84%	80%	66%
10C	SG 5 0.2	--	50%	44%	-- ¹
10D	SG 5 0.2	0.26	46%	42%	-- ¹
10E	PI 240 0.2	--	83%	-- ²	76%
10F	PI 240 0.2	0.26	94%	-- ²	88%

¹ Data was not measured because of the severe color degradation

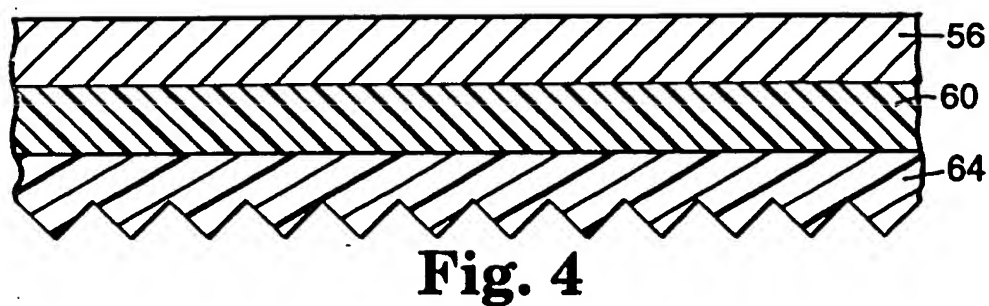
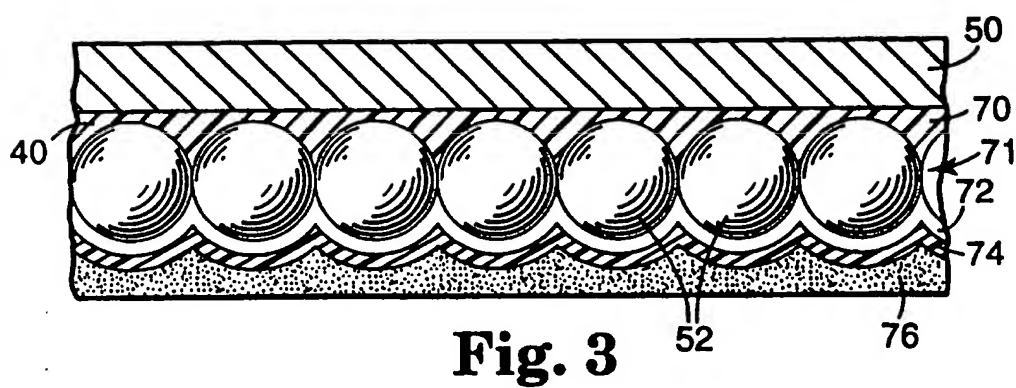
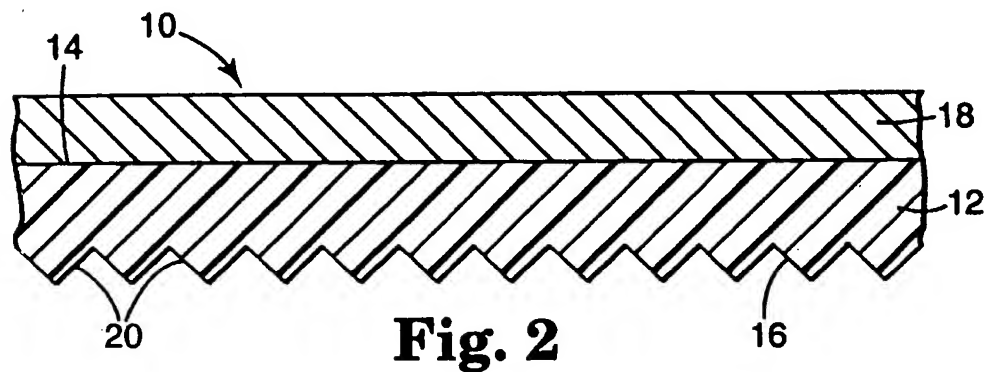
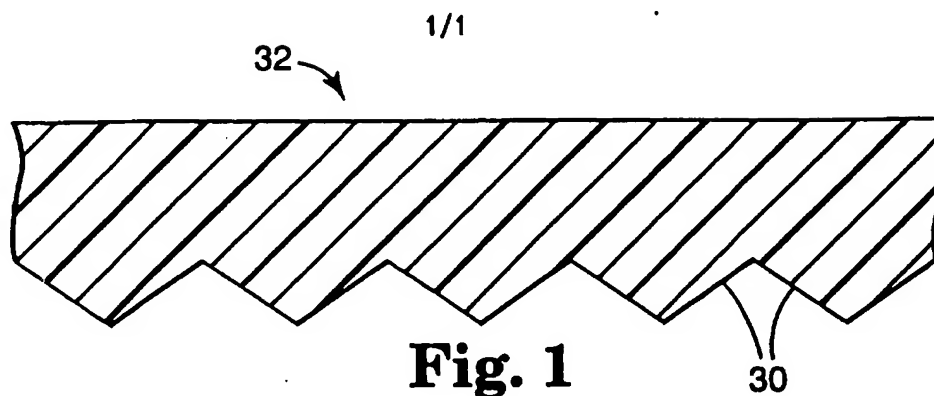
5 ² Samples were not measured at 1500 hour interval.

One skilled in the art will recognize that details of the previous embodiment may be varied without departing from the spirit and scope of the invention.

We claim:

1. An article exhibiting durable color and/or fluorescent properties
5 comprising polymeric matrix, dye and hindered amine light stabilizer, wherein the dye contains at least one of the dyes selected from the group of thioxanthone, perylene imide and thiondigoid compounds and polymeric matrix comprises polycarbonate.
- 10 2. The article of claim 1 wherein the article is retroreflective.
3. The article of claim 1 wherein the article is a film.
4. The article of claim 1 wherein the article contains about 0.01 to
15 about 2.00 weight percent of said dye.
5. The article of claim 1 wherein said article contains about 0.10 to about 0.75 weight percent of said hindered amine light stabilizer.
- 20 6. The article of claim 1 wherein said hindered amine stabilizer is comprised of a 2,2,6,6-tetramethyl piperidine compound.
7. A method of manufacturing an article exhibiting durable color and/or fluorescent properties, comprising:
25 extruding a polycarbonate matrix comprising about 0.01 to about 2.0 weight percent of at least one dye selected from the group consisting of thioxanthone, perylene imide, and thioindigoid compounds and about 0.05 to about 1.00 weight percent of a hindered amine light stabilizer.

8. The method of claim 7 wherein the hindered amine light stabilizer is comprised of a compound from the class of 2,2,6,6 tetramethyl piperidine compounds.
- 5 9. A method of increasing the durability of polycarbonate comprising combining polycarbonate with hindered amine light stabilizer and dye wherein the dye contains at least one of the dyes selected from the group of thioxanthone, perylene imide and thioindigoid compounds.
- 10 10. The method of claim 9 wherein the hindered amine light stabilizer is a 2,2,6,6-tetramethyl piperidine compound.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/13340

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K5/3435 C09B67/00 B44F1/04 G09F13/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B44F C08K C09B G09F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 612 796 (CIBA GEIGY AG) 31 August 1994 see page 2, line 1 - page 9, line 37	1,3-10
Y	---	2
Y	EP,A,0 489 561 (MINNESOTA MINING AND MANUFACTURING COMPANY) 10 June 1992 cited in the application see page 2, line 55 - page 4, line 43	2
X	US,A,5 302 497 (GODWIN BERNER ET AL) 12 April 1994 see column 1, line 1 - column 8, line 25	1,3,6,9, 10
P,X	EP,A,0 637 493 (NORDICA S.P.A.) 8 February 1995 see column 2, line 23 - column 3, line 50	1,3,4,6, 9,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-612796	31-08-94	CA-A- 2116063	24-08-94
		JP-A- 6256678	13-09-94
EP-A-489561	10-06-92	AT-T- 134947	15-03-96
		AU-B- 645626	20-01-94
		AU-B- 8779591	11-06-92
		CA-A- 2055194	07-06-92
		JP-A- 4292940	16-10-92
		US-A- 5387458	07-02-95
US-A-5302497	12-04-94	CA-A- 2032692	22-06-91
		EP-A- 0436464	10-07-91
		JP-A- 8012893	16-01-96
EP-A-637493	08-02-95	JP-A- 7088891	04-04-95